

## WEST Search History





DATE: Monday, February 02, 2004

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<input type="checkbox"/>	L29	l27 and L28	148
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<input type="checkbox"/>	L27	l6 and L26	436
<input type="checkbox"/>	L26	l1 same L25	1023
<input type="checkbox"/>	L25	trivalent chromium	2656
<input type="checkbox"/>	L24	l1 and L23	15
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<input type="checkbox"/>	L2	bismuth or bi	469207
<input type="checkbox"/>	L1	hexavalent chromium	4033

END OF SEARCH HISTORY

[54] REMOVAL OF HEAVY METAL IONS FROM PLATING WASTES

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[73] Assignee: Schlage Lock Company, San Francisco, Calif.

[22] Filed: Oct. 24, 1972

[21] Appl. No.: 300,133

[52] U.S. Cl. .... 210/53, 134/13

[51] Int. Cl. .... C02c 5/02

[58] Field of Search .... 210/50, 53, 42, 51, 52, 210/47, 59, 60; 423/596, 597; 134/13

[56]

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Hoover et al., "Disposal of Waste Liquors from Chromium Plating," Industrial & Engineering Chemistry,

Vol. 33, No. 1, January, 1941, pp. 131-134.

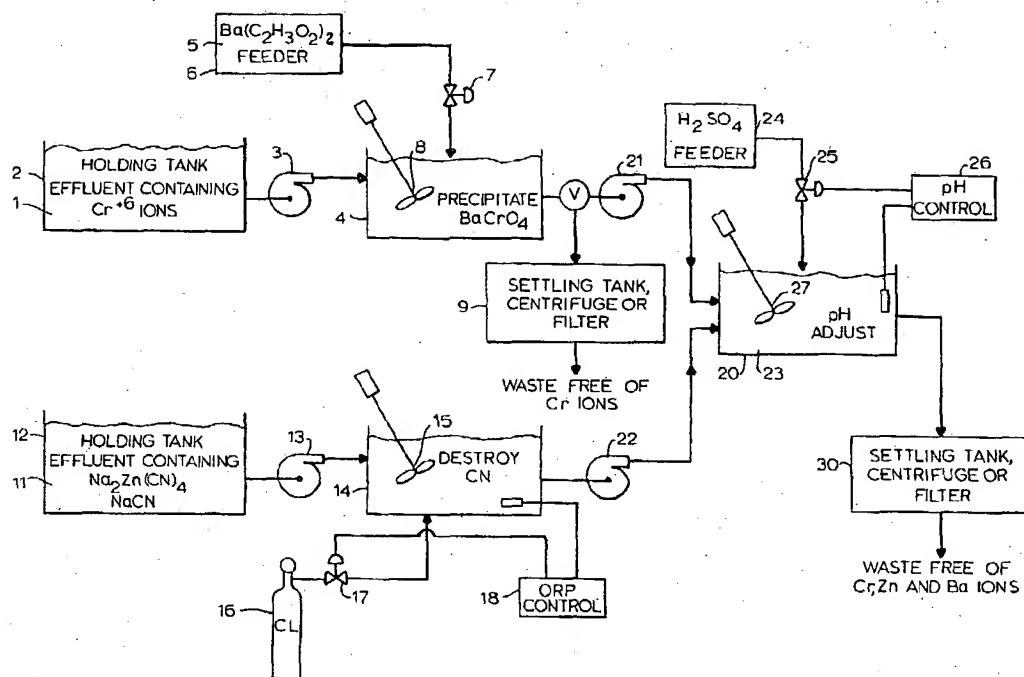
Primary Examiner—Thomas G. Wyse  
Attorney, Agent, or Firm—Owen, Wickersham & Erickson

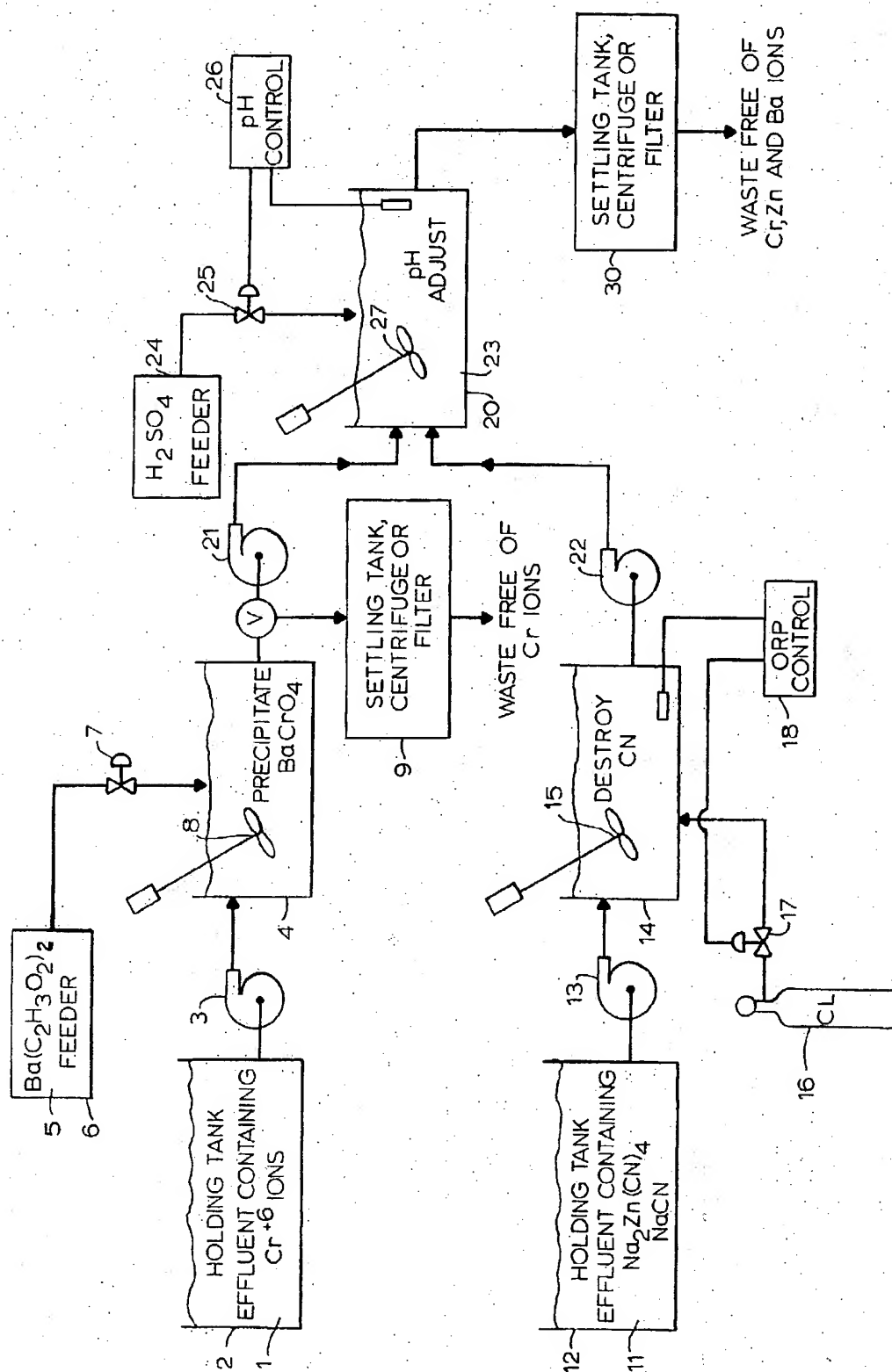
[57]

## ABSTRACT

Treatment of plating effluents, including at least chromium plating effluent and, in plants having it, zinc plating effluent as well as effluents from plating copper, cadmium, or nickel, removing from these effluents the heavy metal ions. Hexavalent chromium ions are removed directly, without first reducing them to trivalent forms, by adding barium acetate. When other plating effluents are treated, the formed barium compounds are used as a coagulant for their hydroxides, which may be formed by mixing any of these other effluents with the formed barium compound and adjusting the pH to the value enabling precipitation of the hydroxides. Sulfuric acid may be used for this pH adjustment, thereby also precipitating out any remaining barium ions in solution.

14 Claims, 1 Drawing Figure





# REMOVAL OF HEAVY METAL IONS FROM PLATING WASTES

## BACKGROUND OF THE INVENTION

This invention relates to the treatment of wastes from electroplating plants for reducing the amount of pollutants in the effluents and removing the heavy metal ions therefrom.

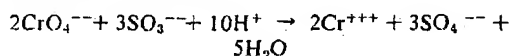
In recent decades there has been a considerable increase in the volume of industrial effluents being discharged into sewers, resulting in pollution of streams, rivers, lakes, underground waters and oceans. This pollution has made it necessary to place restrictions upon uncontrolled effluent disposal, and at the present time the discharge of industrial effluents is coming under the strict control of local and federal authorities.

Metal-finishing industries have to dispose of dilute effluents containing highly toxic heavy metal ions. Solutions such as electroplating plant effluents containing intolerable quantities of chromium and zinc ions are difficult to dispose of safely.

Presently known methods of removal of these heavy metal ions from plant effluents have been wasteful of land, for they have required large areas for settling tanks or ponds, due to the slow settling rates of the voluminous and gelatinous metal compounds that were precipitated from effluent solutions treated by these prior-art methods.

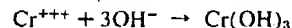
Other known methods that have been proposed call for expensive proprietary chemicals or expensive proprietary integral process and equipment or both, and some of these methods do not offer complete removal of toxic ions from the treated solutions. Moreover, the commonly known methods have often required a number of consecutive chemical processes in order to obtain the end in view.

For example, effluent containing chromic acid, which is a compound of hexavalent chromium, has commonly been treated first by chemically reducing the hexavalent chromium ions to a trivalent form and then by precipitating the trivalent chromium as chromic hydroxide. However, reduction of hexavalent chromium is efficient and complete only when done at pH 2.0 to 2.5. Hence, the process of reduction has required adjustment of the pH of the collected effluents prior to the reduction process. Various strong reducing agents such as sulfur dioxide, sulfurous acid, sodium sulfite, sodium bisulfite, ferrous sulfate or metallic iron have been used. For example:



This reaction requires theoretically 96 pounds of sulfur dioxide to reduce 100 pounds of chromic acid. Alternatively, 100 pounds of chromic acid would theoretically require either (1) 156 pounds of sodium bisulfite plus 74 pounds of sulfuric acid, or (2) 190 pounds of sodium sulfite plus 147 pounds of sulfuric acid, or (3) 843 pounds of ferrous sulfate plus 294 pounds of sulfuric acid. So the reduction process of chromic acid to trivalent chromium has required large quantities of reagents and adequate equipment, and has therefore been expensive.

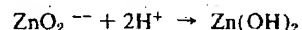
The second step in this prior-art process was the precipitation of trivalent chromium ions as chromic hydroxide:



using alkali hydroxides such as sodium hydroxide, sodium carbonate, or calcium hydroxide. The most common practice has been to use sodium hydroxide as the precipitant, but the resultant precipitate is soluble in an excess of the reagent, and precipitation is possible only after hydrolysis accomplished by prolonged boiling with a considerable amount of water; even then precipitation is always incomplete.

This same prior-art process required considerable time and large installations. For this reaction, to treat 100 pounds of chromic acid (after reduction) it has taken 120 pounds of sodium hydroxide or 159 pounds of sodium carbonate, or 111 pounds of calcium hydroxide, to assure perfect stoichiometric reaction. So precipitation, as well as reduction, has also been expensive. Precipitated chromic hydroxide is exceptionally voluminous and has very poor settling properties. Poor coagulation of the precipitate may be improved by adding suitable coagulating agents, such as by adding expensive polyelectrolytes or by adding ferric compounds, which would require additional quantities of precipitant. Thus the process was expensive at every stage.

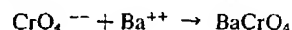
The effluents from most plating plants also contain zinc ions as a waste from zinc electroplating processes. In the majority of cases, zinc is plated by cyanide zinc plating processes. The effluent from the zinc cyanide process must first be treated to destroy the cyanide ions by oxidizing them to carbon dioxide and nitrogen. The oxidation is carried out at pH 10 to 11.5, in most cases using chlorine as the oxidizing agent. The effluent, once free from cyanides, contains sodium zincate  $\text{Na}_2\text{ZnO}_2$ . The conventional method for precipitating zinc from a sodium zincate solution has been by lowering the pH to a value of pH  $8.0 \pm 0.2$  in order to precipitate zinc hydroxide. Zinc hydroxide is amphoteric, but within these narrow limits of pH value the precipitation of zinc hydroxide is quantitative:



The precipitated zinc hydroxide is gelatinous, voluminous, has very poor settling properties, and is difficult to filter.

## SUMMARY OF THE INVENTION

In this invention, the effluents from electroplating plants containing chromic acid  $\text{Cr}^{+6}$  or dichromates  $\text{Cr}^{+6}$  or mixture of both are precipitated by barium acetate as crystalline barium chromate:



or



The precipitation is instant, settling is rapid, the precipitate is compact, and if necessary, the precipitate can be readily filtered.  $\text{BaCrO}_4$  after 15 minutes of settling time is more definitely separated than is  $\text{Cr}(\text{OH})_3$ , yet it occupies only about one-third as much volume as the precipitated  $\text{Cr}(\text{OH})_3$  after 15 minutes of settling. After a settling time of 1 hour, the volume of precipitated  $\text{BaCrO}_4$  is about one-seventh the volume of precipitated  $\text{Cr}(\text{OH})_3$ , yet the  $\text{BaCrO}_4$  is almost completely settled whereas the  $\text{Cr}(\text{OH})_3$  can stand for weeks without fully settling.

In plants where there is zinc plating, the effluent containing the precipitated barium chromate may be mixed with effluents containing sodium zincate. The mixture of both effluents has a pH of about 11.0. The value of the pH can be adjusted to and maintained at pH  $8.0 \pm 0.2$  in order to precipitate the zinc hydroxide.

The settling of the combined precipitates of barium chromate and zinc hydroxide is rapid and is compact. After 1 hour of sedimentation, when its settlement is nearly complete, the volume of the mixed precipitates though further advanced in separation occupy only about 30 percent as much volume as do precipitates of chromic hydroxide and zinc hydroxide after settling for 6 hours. The filtering of the mixed precipitates of barium chromate and zinc hydroxide is easily performed, and the drying time of the sludge is greatly reduced.

#### BRIEF DESCRIPTION OF THE DRAWING

The drawing is a flow sheet of a method embodying the principles of the invention.

#### DESCRIPTION OF A PREFERRED EMBODIMENT

The precipitation of chromic acid as barium chromate by various water-soluble barium compounds can be carried out from an alkaline solution of chromic acid but cannot usually be carried out from dichromates unless an alkali acetate is added. Barium acetate is an exception to this rule, for it quantitatively precipitates barium chromate from both chromic acid and dichromates from neutral or slightly acid solutions.

As shown in the drawing, effluent 1 containing hexavalent chromium may be collected in a holding tank 2 where the effluent from chromium plating operations containing dilute chromic acid  $\text{Cr}^{+6}$  may be combined with dichromates  $\text{Cr}^{+6}$  from other operations in the plating plant such as chemical conversion coatings, etc. in any combination. The effluent 1 is moved from the tank 2 by a pump 3 to a precipitation tank 4, where a metered amount of barium acetate solution 5 from a tank 6 is added to the chromium plating effluent via a valve 7, which may do the metering. Preferably, the solution in the tank 4 is agitated by a mixer 8. The addition of the barium acetate solution 5 causes a precipitate of barium chromate, acetic acid being the remaining component. Theoretically the barium acetate and chromic acid or dichromate can be completely reacted by calculating the exact amounts, but as a matter of practicality it is normal to add a slight excess of the barium acetate to insure precipitation of all the chromium. The precipitation is instant, and the material rapidly settles.

If desired, this particular precipitation reaction can be completed (see box 9) by simply filtering out or centrifuging out the barium chromate or by letting it settle in a settling tank and then disposing of the remaining solution as by decanting. If an excess of the barium acetate has been used, the filtrate or decanted liquid can then be treated with sulfuric acid or sodium sulfate to precipitate the remaining barium ions so that the effluent will also be free of barium. If settling is used, a retention time of 2 hours is preferably allowed. If the plating plant does not do any zinc plating, this completes the method, and this process has the following advantages over prior methods:

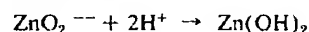
1. Precipitation is much more rapid.
2. The volume of the precipitate is much smaller and more easily filtered or disposed of.

3. Rapid turnover is possible, affording treatment of a large amount of solution in a relatively short time in a relatively small area.

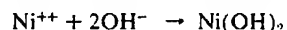
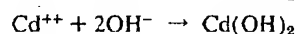
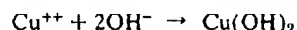
4. No reduction of hexavalent chromium is required.

If the plating plant is one that also does zinc plating, then the solution of sodium zincate as described earlier is now mixed with the solution containing already precipitated barium chromate. Thus, an effluent 11 of sodium zinc cyanide, with free sodium cyanide is collected in a tank 12 and moved by a pump 13 to a treatment vessel 14 having an agitator 15. There, the cyanide ions are destroyed by oxidation, as with chlorine from a vessel 16, fed into the vessel 14 through a valve 17, oxidation-reduction potential being controlled by a suitable well-known control device 18. The effluents from the tanks 4 and 14 are sent to a tank 20 by pumps 21 and 22.

The mixture 23 of these two effluents is then treated with sulfuric acid to adjust the pH of the mixture to pH  $8.0 \pm 0.2$  as determined by a pH control device 26. A mixer 27 assures good mixing of the effluent mixture with sulfuric acid introduced from a container 24 via a valve 25. Sulfuric acid has the advantage that there is no need to add any other materials to help precipitate the remaining barium ions that have been added in excess to assure quantitative precipitation of barium chromate. When sulfuric acid is used, it will first precipitate out barium as insoluble barium sulfate, and the remainder of it is used to react with sodium zincate to produce zinc hydroxide:



At the same time any other metal ions commonly used in electroplating operations and therefore present in plant effluent such as copper, cadmium and nickel can be precipitated out as metal hydroxides:



Effluents containing these metals may be treated along with the zinc cyanide, if they are cyanides, or otherwise may be sent directly to the tank 20. As stated earlier, the settling of the combined precipitates (barium chromate, barium sulfate, zinc hydroxide and all other metal hydroxides) is rapid due to the fact that the barium chromate and barium sulfate act as an excellent coagulant for the metal hydroxides, particularly the most difficult to filter, zinc hydroxide, which is especially voluminous and gelatinous.

Once again the effluent is sent to a separator device 30 such as a settling tank, filter or centrifuge.

A comparison of certain aspects of the present invention with corresponding aspects of the prior art are being set forth in tabular form:

Table 1

Some Comparative Characteristics of Chromium Precipitates	$\text{Cr(OH)}_3$	$\text{BaCrO}_4$
	amorphous	crystalline
Structure	7	1
Sedimentation — time unit	7.5	1
Volume unit	not practical	convenient
Decantation	poor	excellent
Filtration		
Filtered sludge drying — time unit	5	1

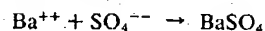
Table 2

	Some Comparative Characteristics of Combined Precipitates of Chromium and Zinc	
	$\text{Cr}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$	$\text{BaCrO}_4$ and $\text{Zn}(\text{OH})_2$
Structure	amorphous — gelatinous	coagulated
Sedimentation — time unit	5	1
Volume unit	3	1
Decantation	not practical	convenient
Filtration	poor	excellent
Filtered sludge drying — time unit	4	1

The filtrate contains sodium acetate, sodium sulfate and sodium chloride. These materials are acceptable to most sanitary sewer systems.

#### EXAMPLE 1

A thousand gallons of dilute effluent from the process containing what is considered to be a maximum concentration under normal operating conditions containing an estimated amount of 5 pounds of chromic acid or 600 ppm  $\text{CrO}_3$  is treated with 60 gallons of water solution containing 12.5 pounds of barium acetate  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ . The material is mixed thoroughly and the precipitate is very rapidly formed. The barium acetate is added in slight excess. To remove the excess barium ions, about one pound of sodium sulfate  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is added:



After settling for about 1 hour the contents of the tank are decanted and filtered, and the filtrate containing sodium acetate, and sodium sulfate goes to the sewer. The sludge containing water insoluble barium chromate  $\text{BaCrO}_4$  and barium sulfate  $\text{BaSO}_4$  is dried and disposed of as land fill.

#### EXAMPLE 2

A chromium plating effluent containing chromic acid joined by other streams containing dichromates from other processes and a separate stream carrying wastes from a zinc plating operation is treated as follows:

1,000 Gallons of dilute effluent containing chromic acid and dichromates totaling 600 ppm of hexavalent chromium, calculated as  $\text{CrO}_3$  in the amount of 5 pounds, is treated with 60 gallons of water containing 12.5 pounds barium acetate. The material is mixed thoroughly and the precipitate of barium chromate is immediately formed. At this point 1,000 gallons of alkaline effluent, containing sodium zincate (after the destruction of cyanides) and having a pH value of about 11.0 and containing a typical maximum of 50 ppm of zinc, is added to the tank which contains the precipitated barium chromate. The pH value of the mixture is adjusted to  $\text{pH } 8.0 \pm 0.2$  by adding approximately 8 pounds of sulfuric acid and is agitated. As stated earlier, the settling of combined precipitates of barium chromate, barium sulfate and zinc hydroxide is rapid, due to the fact that the barium chromate and barium sulfate act as an excellent coagulant for gelatinous and voluminous zinc hydroxide. After settling for 1 hour, the contents of the tank are decanted and filtered. The filtrate containing sodium chloride, sodium sulfate and sodium acetate goes to the sewer. The sludge containing water-insoluble barium chromate, barium sulfate and zinc hydroxide is dried and disposed of as land fill.

#### EXAMPLE 3

When the plating plant is one that also does cadmium cyanide and copper cyanide plating as well as chromium plating and zinc cyanide plating, the combined dilute wastes from all cyanide processes are treated together by chlorination process in order to destroy cyanides. After destruction of cyanides is accomplished, a thousand gallons of the alkaline effluents, pH about 11.0, containing zinc plus copper (typical average concentration 50 ppm), and cadmium (typical average concentration 50 ppm) were added to the tank which contains the precipitated barium chromate. The pH value of the mixture is adjusted to  $\text{pH } 8.0 \pm 0.2$  by adding approximately 8 pounds of sulfuric acid and is agitated. After settling for 1 hour, the contents of the tank are decanted and filtered. The filtrate containing sodium chloride, sodium sulfate and sodium acetate goes to the sewer. The sludge containing water-insoluble barium chromate, barium sulfate, zinc hydroxide, cadmium hydroxide and copper hydroxide is dried and disposed of as land fill.

#### EXAMPLE 4

When the plating plant is one that does chromium plating, zinc cyanide plating, cadmium cyanide plating, copper cyanide plating and also nickel plating, then a separate stream of dilute wastes from the nickel plating process is directly added to the tank with precipitated barium chromate. The dilute wastes from the nickel plating have average Ni concentration of 20-100 ppm and the pH value is in the range of pH 6-7. The adjustment of the pH value of the total mixture is exactly the same as described in Example No. 3. After agitation, followed by settling for one hour, the contents of the tank are decanted and filtered. The filtrate containing sodium chloride, sodium sulfate and sodium acetate goes to the sewer. The perfectly coagulated sludge containing water-insoluble barium chromate, barium sulfate, hydroxides of zinc, cadmium and copper and also quantitatively precipitated and water-insoluble nickel hydroxide is dried and disposed of as land fill.

I claim:

1. A process for treating plating plant effluent containing hexavalent chromium ions to remove the chromium ions comprising adding thereto barium acetate in an amount sufficient to precipitate substantially all of the hexavalent chromium ions as barium chromate and separating the barium chromate precipitate from the solution, to provide a solution from which the chromium ions have been quantitatively removed.
2. The process of claim 1, including adding after completing the addition of barium acetate a solution containing a substance chosen from the group consisting of sulfuric acid and water-

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soluble sulfates in a slight excess, sufficient to precipitate the barium ions, and separating the barium sulfate precipitate from the solution.

3. The process of claim 2, wherein said substance is added before the step separating the barium chromate but after precipitating the barium chromate, and both the barium chromate and barium sulfate are separated simultaneously from the solution.

4. The process of claim 3 wherein the separating is done by settling and decanting.

5. The process of claim 3 wherein the separating step is done by filtration.

6. The process of claim 3, including adding a second plating effluent containing other heavy metal ions after the barium acetate has been added and mixed and before the separating step, and adjusting the pH of the mixture before separation so as to precipitate the hydroxide of the other heavy metal ions, said barium chromate and barium sulfate being used as coagulants to hasten separation of the precipitated hydroxides from the solution.

7. The process of claim 6 wherein said second plating effluent contains at least one metal chosen from the group consisting of zinc, copper, nickel, and cadmium.

8. A process for treating plating plant aqueous effluent containing hexavalent chromium ions as a soluble compound chosen from the group consisting of chromic acid and alkali metal and ammonium bichromates, to remove the chromium ions, comprising sequentially adding thereto an aqueous solution of barium acetate in an amount sufficient to precipitate substantially all of the hexavalent chromium ions as barium chromate,

adding thereto in aqueous solution a substance chosen from the group consisting of sulfuric acid and the water-soluble sulfates in an amount sufficient to precipitate all remaining barium ions in solution as barium sulfate, and

separating the barium chromate and barium sulfate precipitates from the solution, leaving a solution that can be disposed of more safely than the original said effluent.

9. The process of claim 8, including adding, after the step of adding the barium acetate

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and before the step of separating, at least one other plating effluent containing metal ions of at least one metal chosen from the groups consisting of zinc, nickel, copper, and cadmium, and

adjusting the pH of the resulting mixtures to an amount where the hydroxide of each said metal can precipitate,

said barium chromate and barium sulfate serving as coagulants for such hydroxide.

10. A process for treating aqueous plating plant effluents, in which there is a first effluent containing hexavalent chromium ions and a second effluent containing zinc ions that have been converted to sodium zincate, comprising the following steps:

adding a solution of barium acetate to said first effluent in an amount sufficient to precipitate substantially all of the hexavalent chromium ions as barium chromate,

mixing the resultant mixtures with said second effluent,

adjusting the pH of this mixture of effluents to pH 8, to precipitate zinc hydroxide,

said barium chromate acting as a coagulant to hasten coagulation of the zinc hydroxide and

separating the precipitates barium chromate and zinc hydroxide from the solution.

11. The process of claim 10, adding after completing addition of the barium acetate a substance chosen from sulfuric acid and the soluble sulfates in aqueous solution, to precipitate any barium ions remaining and in solution,

removing the precipitate therefrom.

12. The process of claim 10 wherein said pH is adjusted to pH 8 by sulfuric acid, thereby also precipitating as barium sulfate and barium ions remaining in solution.

13. The process of claim 12, including adding at about the same time as said second effluent a third plating effluent containing at least one soluble salt of at least one metal chosen from the group consisting of copper, cadmium, and nickel.

14. The process of claim 10 wherein the separating comprises settling for at least one hour and then decanting, filtering the decanted liquid.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 3,869,386  
DATED : March 4, 1975  
INVENTOR(S) : Wladyslaw Izdebski

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 35, which is line 3 of claim 12,  
"and barium ions" should read --any barium ions--.

Signed and sealed this 6th day of May 1975.

(SEAL)  
Attest:

RUTH C. MASON  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents  
and Trademarks

# United States Patent

[11] 3,616,344

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Theodore H. Dexter, Lewiston, both of N.Y.  
[21] Appl. No. 697,595  
[22] Filed Jan. 15, 1968  
[45] Patented Oct. 26, 1971  
[73] Assignee Hooker Chemical Corporation  
Niagara Falls, N.Y.

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Primary Examiner—Wyman: Daniel E.  
Assistant Examiner—P. E. Konopka  
Attorneys—Peter F. Casella, Richard K. Jackson, Donald C.  
Studley, Richard P. Mueller and James F. Mudd

[54] **ELECTROCHEMICAL MACHINING WITH FIRE-  
RETARDANT SODIUM CHLORATE  
COMPOSITIONS**  
6 Claims, No Drawings

[52] U.S. Cl. .... 204/143 M,  
23/56, 156/19, 252/8.1, 252/79.1, 252/79.5,  
204/145  
[51] Int. Cl. .... B23p 1/00  
[50] Field of Search ..... 204/145,  
143, 141; 156/19, 18; 252/186, 187; 134/2, 10, 13;  
148/6, 14; 23/45, 56, 57

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2,110,187 3/1938 Williams ..... 23/56  
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**ABSTRACT:** The hexavalent chromium content of aqueous chlorate-containing electrolyte solution employed in electrochemical machining or grinding operations may be reduced through reduction to the trivalent chromium state from which it will precipitate as hydrous chromic oxide or by removal in the hexavalent state by precipitation as a barium, lead, zinc, cobalt or copper salt. The removal of trace hexavalent chromium values from a chlorate-containing electrochemical machining electrolytic solution reduces the fire hazard attending the use of chlorate-containing solutions which may accidentally wet an organic material such as an operator's clothing and subsequently dry to form an extremely combustible mixture. Likewise, the removal of trace hexavalent chromium values from an aqueous chlorate-containing solution reestablishes the flame-retardant activity of an additive such as sodium metasilicate or sodium hydroxide which activity is reduced in the presence of trace hexavalent chromium ions.

# 1

## ELECTROCHEMICAL MACHINING WITH FIRE-RETARDANT SODIUM CHLORATE COMPOSITIONS

### BACKGROUND OF THE INVENTION

Alkali metal and ammonium chlorates, especially sodium chlorate, are ideal electrolytes for use in electrochemical machining operations. The major problem attending their use resides in their tendency to rapidly oxidize combustible materials. The advantages and problems residing in the use of chlorates as the electrolyte in electrochemical machining operations are summarized in the article appearing in *Metal Progress*, March 1967, pp. 81-84. For example, when some of the chlorate-containing electrolyte comes into contact with the clothing of the operator, or any combustible material near an electrochemical machining operation, the tendency to initiate fire is great after the wetted material has dried.

By electrochemical machining operations it is intended to include those operations by which a workpiece is machined, milled, or ground so that the metal is removed by an electrochemical process to produce shaped or curved structures. Likewise, those electrochemical processes by which a hole is bored into or through a workpiece or the surface of a workpiece is smoothed is embraced by the expression electrochemical machining operations. The workpiece to be shaped functions as the anode in electrically conducting relationship with the cathode die through a suitable electrolyte. Some electrolytes used in electrochemical machining are described in U.S. Pat. No. 2,798,846 to Comstock, issued July 9, 1957 as  $\text{NaNO}_3$ ,  $\text{Na}_2\text{CrO}_4$ ,  $\text{KNO}_3$ ,  $\text{K}_2\text{CrO}_4$ , the amines of sodium nitrate, sodium and potassium dichromate, sodium and potassium chlorate and sodium and potassium chlorite. Essentially, the selection of the electrolyte is based upon its conducting properties, its tendency to attack the electrodes, its performance in electrochemical machining operations and its cost. Comstock mentions the rusting of a workpiece and its prevention through the use of a rust-inhibiting agent as the electrolyte.

Electrochemical machining or grinding embraces those procedures which employ a metal or metalloid material as a workpiece from which material is to be removed via electrolytic attack. The workpiece is the anode while the die or grinding wheel is connected as the cathode and the electrical circuit is completed from anode to cathode by the electrolyte (alkali metal or ammonium chlorate). The electrolyte may be directed into the work gap through the cathode if a hollow electrode is employed or the electrolyte may be presented to the work gap by any means known to the art. The solution of electrolyte is held in a reservoir from which it may be fed to the work gap and back to the holding reservoir. Sludge which forms in the electrolyte solution will slowly settle out in the holding reservoir yielding a thickened slurry which may be removed by filtration.

Sodium chlorate is an excellent electrolyte for electrochemical machining operations. Sodium chlorate solutions used as the electrolyte in electrochemical machining are typically aqueous solutions containing about 350 grams per liter  $\text{Na}_2\text{Cr}_2\text{O}_7$ . A typical solution is one containing 3 pounds of sodium chlorate per gallon, which is equal to 359 grams per liter. Hence, a typical electrochemical machining electrolyte may be considered to be an aqueous solution containing from about 300 to 400 grams sodium chlorate per liter. The used electrolyte solutions, usually of pH above about 6 to 7, contain precipitated hydroxides of the metal removed from the workpiece. For example, where the workpiece contains iron, nickel or chromium, the corresponding iron, nickel or chromium hydroxides are formed.

In the electrochemical machining of chromium-containing alloys, some soluble sodium chromate is introduced into the sodium chlorate electrolyte. The introduction of trace amounts (normally between about 0.02 to 2.0 grams as Cr per liter) of sodium chromate into the electrolyte actually increases the fire hazard attending the chlorate and its action on combustible organic material. Hence, any flame-retardant ad-

ditive will have to function in the presence of at least low concentrations of dissolved  $\text{CrO}_4^{2-}$  ions. It is also important that any additive must not change the characteristics of sodium chlorate in its operation as an electrolyte. However, it is most desirable that an additive both act as a flame retardant and improve, or not impair the properties of sodium chlorate as an electrolyte.

Actually, in a standard testing procedure, where the burning time of a cotton twill strip 1.5 inch wide and 52 inches in length is determined, the burning time for untreated cloth is about 36 seconds, whereas the burning time for the corresponding cloth which has been dried after impregnation with about 1 gram of sodium chlorate solution per gram of cloth under conditions of controlled humidity at room temperature, will vary from about 6 seconds to about 12.6 seconds, based upon the relative humidity of the drying atmosphere of 20 percent for the former and about 52 percent for the latter. As the amount of hexavalent chromium present with the chlorate increases, the burning time for the test cloth dried at 20 percent relative humidity will increase to 4.1 seconds at 0.05 gram  $\text{Cr}^{+6}$  per liter; to 3.2 seconds at 0.1 gram  $\text{Cr}^{+6}$  per liter; to 1.9 seconds at from 0.5 to 2.0 grams  $\text{Cr}^{+6}$  per liter.

It has recently been discovered that flame-retardant additives may be included with an alkali metal or ammonium chlorate as the electrolyte solution in electrochemical machining and grinding operations. The flame-retardant additives such as sodium metasilicate and sodium hydroxide greatly reduce the burning time of cotton cloth which has been wetted with a chlorate-containing solution and subsequently dried. However, this flame-retarding influence is somewhat diminished when hexavalent chromium is introduced into the electrolyte solution form oxidized chromium metal found in alloys machined by electrochemical techniques.

It is an object of this invention to decrease the fire hazard attending the use of chlorate-containing solutions when organic matter is wetted by such a solution and dried.

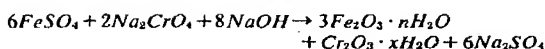
It is an additional object of this invention to reestablish the fire-retardant ability of such additives as sodium metasilicate and sodium hydroxide incorporated into chlorate-containing electrolytic solutions for use in electrochemical machining and grinding operations.

### DETAILED DESCRIPTION OF THE INVENTION

In accordance with this invention, it has been discovered that the fire-accelerating effect of chlorate-induced combustion created by the presence of trace hexavalent chromium ions in an aqueous chlorate-containing solution may be avoided by reduction or removal of the hexavalent chromium ions.

More specifically, it has been found that the hexavalent chromium ion content, which is introduced into the aqueous sodium chlorate electrolyte solution employed to electrochemically machine a metal alloy containing chromium by oxidation of the chromium metal to the hexavalent chromium state (e.g.  $\text{CrO}_4^{2-}$ ), may be removed by the regular addition of a reducing agent such as an alkali metal or ammonium sulfide, stannous salts such as  $\text{SnSO}_4$ ,  $\text{SnCl}_2$ , and the ferrous salts such as  $\text{FeSO}_4$ ,  $\text{FeCl}_2$ , and  $\text{Fe}(\text{NO}_3)_2$  to the chlorate-chromate-containing solution to reduce the chromate ion to the trivalent chromium valence state in which state the chromium precipitates from solution as hydrous chromic oxide. The reducing agent must not react with the alkali metal or ammonium chlorate in the aqueous solution under the electrolytic conditions employed (i.e. above pH 6 with from about 300 to 400 grams  $\text{NaClO}_3$  per liter).

An especially applicable and the preferred reducing agent is the ferrous  $\text{Fe}^{+2}$  ion, added to the hexavalent chromium-ion-containing solution as a soluble salt, such as the chloride, sulfate or nitrate. An alkali may be added in combination with the ferrous salt to prevent acidification of the electrolyte solution through formation of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , etc. coming from the ferrous salt. The overall reaction involved in this process taking place in aqueous solution may be noted as:



The values of  $n$  and  $x$  vary with conditions of the precipitation. The hydrous oxides of  $\text{Fe}^{+3}$  and  $\text{Cr}^{+3}$  thus formed are the same type of compound as the metal hydroxides or hydrous oxides comprising the sludge normally encountered in electrochemical machining operations and the  $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  does not noticeably accelerate the burning of cloth when wetted with the chlorate solution, dried and ignited. The hydrous oxides of  $\text{Fe}^{+3}$  and  $\text{Cr}^{+3}$  may then be removed from the electrolytic solution along with the sludge derived from the metal coming from the machining of the workpiece by filtration or some other applicable procedure known to the art. After this treatment, only a few parts per million of hexavalent chromium ions remain dissolved in the electrolyte.

The addition of a reducing agent to the hexavalent chromium-containing electrolyte may be made at any stage of an electrochemical machining operation. The hydrous chromium oxide and hydrous iron oxide will remain in suspension in the aqueous electrolyte along with the metal hydroxides or hydrous oxides formed during the machining operation until they are removed by known methods such as filtration. However, it is preferred to add the reducing agent to the aqueous electrolyte just prior to the sludge removal step in the electrochemical machining or grinding cycle. The reducing agent may be well mixed with the electrolyte to afford the optimum reduction of hexavalent chromium. By this procedure, the hexavalent chromium level may be maintained at a very low level in the chlorate electrolyte solution.

If it is not desirable to employ a reducing agent to remove trace amount of hexavalent chromium ions from the chlorate-containing solution, the chromate ions may be removed through precipitation of an insoluble chromate salt.

In accordance with this second aspect of the invention, the aqueous chlorate-containing electrolyte solution which has been contaminated by  $\text{Cr}^{+6}$  ions may be treated with a small excess of the required stoichiometric amount of a soluble salt containing a member selected from the group consisting of divalent barium, lead, zinc, cobalt and copper. The anions forming soluble salts with these cations are for example the chlorides, nitrates, etc. However, it is preferred to add these reagents already formulated into an aqueous solution as a nitrate and introduce the reagent in the electrolyte solution just prior to sludge removal so that the  $\text{BaCrO}_4$ ,  $\text{CoCrO}_4$ ,  $\text{PbCrO}_4$ ,  $\text{ZnCrO}_4$ , or  $\text{CuCrO}_4 \cdot \text{CuO}$  precipitate may be removed with the sludge.

Similarly, a low concentration of one or more of the added metal ions could be maintained in the electrolyte solution at all times to precipitate hexavalent chromium ions as they are formed. Barium is the preferred reagent in this situation because it will remain solubilized in an alkaline electrochemical machining electrolyte

#### EXAMPLES I-V

To determine the effect of hexavalent chromium ion removal from chlorate-containing electrochemical machining electrolytes, the following experiments were conducted. In each example, a strip of cotton twill 6 feet by 1.5 inch was soaked in the test solution, wrung out and dried under controlled conditions of 20-percent relative humidity and room temperature. The cloth strips were then hung vertically and ignited at the bottom with a 0.5-inch flame (small source). The time required to burn (or char) a 52-inch section of cloth was determined. In its original state, without treatment, this standard cloth burns in 36 seconds. Hence any treatment of the chlorate-containing electrolyte solution which will prevent the rapid burning that is produced by an alkali metal or ammonium chlorate is an effective fire-retardant treatment. In each test, the cloth strip was loaded with about 1 gram of solution per gram of cloth. Each solution contained 400 grams sodium chlorate per liter. This concentration approximates the usual concentration of chlorate used for electrochemical machining (3 pounds per gallon=359 grams per liter).

#### EXAMPLE I

The burning time for cloth impregnated with unused electrolyte solution containing 400 grams  $\text{NaClO}_3$  per liter and no hexavalent chromium was 6.0 seconds. After this electrolyte was used in electrochemical grinding of 304 stainless steel containing about 20-percent chromium, the chromate concentration of the aqueous electrolyte was about 0.5 gram of chromium per liter and the burning time for cloth impregnated with the resulting solution was 4.1 seconds. When the chromium content of the used electrolyte rose to 0.1 gram per liter the burning time was 3.2 seconds; at 0.5 gram chromium per liter a burning time of 1.9 second was observed.

#### EXAMPLE II

An electrolyte containing 400 grams  $\text{NaClO}_3$  per liter and 12 grams  $\text{NaOH}$  per liter as a flame retardant was employed as the electrolytic solution for an electrochemical grinding operation. The resulting solution contained 0.1 gram chromium per liter as  $\text{CrO}_4^{+2}$  and resulted in a cloth-burning time of 12.5 seconds. To 1 liter of the used solution was added 20 milliliters of an aqueous solution containing 0.97 gram  $\text{FeSO}_4$  (110 percent of theory) and 10 milliliters of an aqueous solution containing 0.34 gram of  $\text{NaOH}$ . After removal of the precipitate, the chlorate-containing solution retained less than 10 parts per million of chromium and gave a burning time of 70 seconds.

#### EXAMPLE III

An electrolyte solution of 400 grams  $\text{NaClO}_3$  per liter and 51 grams per liter of  $\text{Na}_2\text{SiO}_3$  as flame retardant was used for electrochemical grinding as in example II. The final liquid phase acquired 0.5 gram chromium per liter as soluble chromate. As in example II, solutions containing 4.85 grams of  $\text{FeSO}_4$  and 1.7 grams of  $\text{NaOH}$  were added simultaneously but separately. The treated liquid contained less than 10 parts per million chromium and resulted in a cloth-burning time of 250 seconds as compared to a burning time 6.9 seconds for the solution prior to chromium removal when ignited with a 4-inch gas flame (large source).

#### EXAMPLE IV

Under the conditions specified in example II, but without addition of  $\text{FeSO}_4$  or  $\text{NaOH}$ , 0.338 gram of  $\text{Ba}(\text{OH})_2$ , as a 5-percent aqueous solution was added to 1 liter of the used chlorate solution.  $\text{BaCrO}_4$  precipitated leaving less than 10 parts per million of chromium in the liquid phase. The burning time of cloth impregnated with the resulting solution was improved to 70 seconds. The amount of  $\text{Ba}(\text{OH})_2$  added in this example is 105 percent of the amount theoretically needed to precipitate the dissolved hexavalent chromium.

#### EXAMPLE V

Under the conditions specified in Example III, but without addition of  $\text{FeSO}_4$  and  $\text{NaOH}$ , 3.26 grams of  $\text{Pb}(\text{NO}_3)_2$  as a 20-percent aqueous solution was added to 1 liter of the used electrolyte.  $\text{PbCrO}_4$  precipitated and was removed to leave a mother liquor containing less than 5 parts per million of dissolved chromium. The burning time for cloth impregnated by the remaining solution was 250 seconds. The amount of  $\text{Pb}(\text{NO}_3)_2$  added in this example is 105 percent of that theoretically needed to precipitate the dissolved hexavalent chromium.

Having disclosed the invention, it will become apparent to those skilled in the art that obvious modifications may be made which do not depart from the true spirit of this contribution. For example, reducing agents other than ferrous salts may be employed to convert hexavalent chromium ions to the trivalent state. For example, any reducing agent may be employed that does not reduce the sodium chlorate or any flame-retardant additive present in the electrolyte. Likewise other means for removing hexavalent chromium from the aqueous chlorate-containing solution may be used such as various inor-

ganic salts which form insoluble chromates. Therefore, the examples herein presented are intended to be illustrative of the inventive concepts rather than limitations upon the actual scope of this contribution.

What is claimed is:

1. In an electrochemical machining process in which a metal is removed electrochemically from a chromium-containing workpiece by the application of electrical current from a cathode die to the workpiece anode through an aqueous solution containing an electrolyte selected from the group consisting of an alkali metal chlorate and ammonium chlorate, the improvement which comprises reducing organic material combustibility by removing hexavalent chromium ions from said aqueous chlorate-containing solution by introducing into said solution at least one member selected from the group consisting of the soluble salts of divalent Fe, Sn, Ba, CO, Pb, Zn, Cu, an alkali metal sulfide and ammonium sulfide and removing the precipitate.

2. The process of claim 1 in which said hexavalent chromi-

um is reduced to trivalent chromium by the introduction into said aqueous chlorate solution of at least one member selected from the group consisting of an alkali metal sulfide,  $(\text{NH}_4)_2\text{S}$ ,  $\text{FeCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{Fe}(\text{NO}_3)_2$ ,  $\text{SnSO}_4$  and  $\text{SnCl}_2$ .

3. The process of claim 1 in which said hexavalent chromium is reduced by the ferrous salt which is introduced into said chlorate solution with sufficient alkali to neutralize any generated acid.

4. The process of claim 1 in which said hexavalent chromium is precipitated from said aqueous chlorate solution by the introduction of at least one member selected from the group consisting of soluble salts of divalent barium, lead, zinc, cobalt and copper.

5. The process of claim 1 in which said soluble salts are selected from the group consisting of chlorides and nitrates.

6. The process of claim 4 in which said soluble salts are nitrates.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,616,344 Dated October 26, 1971

Inventor(s) John A. Peterson and Theodore H. Dexter

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 2, change " $\text{CrO}_4^{12}$ " to read  $---\text{CrO}_4^{-2}---$ , line 12, the word "bee" should read  $---\text{been}---$ ; line 33, the word "form" should read  $---\text{from}---$ ; line 57, change " $(\text{e.g. CrO}_4^{12})$ " to read  $---(\text{e.g. CrO}_4^{-2})---$ .  
Column 4, line 20, change " $\text{CrO}_4^{12}$ " to read  $---\text{CrO}_4^{-2}---$ .

Signed and sealed this 13th day of June 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents